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IR SPECTROSCOPY OF THE NH_4^+ - ION IN Y-ZEOLITES.

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ABSTRACT: An IR study of the ammonium ion in $NaNH_4Y$- and $NaNH_4CsY$-zeolites was done from 25 °C to 450°C and from 1000 mb to 10^{-2} mb. Infrared active absorption bands of the ammonium ion are shifted by hydrogen bonds between the NH_4^+ ion and neighboring oxigen atoms, accompanied simultaneously by a removal of the degeneration of the vibration modes. Ammonium ion, anhydrous or partially or strong perturbed by water can be distinguished. We propose a model of the ammonium ion interaction with its environs. **Key words:** Y-zeolite, NH_4^+ - ion, IR spectroscopy.

ESPECTROSCOPIA DE IR DEL ION AMONIO EN ZEOLITAS Y.

RESUMEN: Se realizó un estudio de infrarrojo del ion amonio en las zeolitas $NaNH_4Y$ y $NaNH_4CsY$ entre 25 °C y 450 °C, y entre 1000 mb y 10^{-2} mb. Las bandas de absorción activas en infrarrojo del ion amonio fueron desplazadas por los enlaces de hidrógeno entre el ion NH_4^+ y los átomos vecinos de oxígeno; este fenómeno fue acompañado simultáneamente por una supresión de la degeneración de los modos de vibración. Se pudieron distinguir los iones amonio, en forma anhidra o perturbados parcial o fuertemente por agua. Se propone un modelo de interacción del ion amonio con sus alrededores. **Palabras clave:** zeolita Y, ion NH_4^+ , espectroscopía de IR.

INTRODUCTION

Several publications have studied NaH-zeolites formation from ammonium zeolites[9,1,2]. Recently, the first systematic investigation on faujasitic ammonium zeolites was published[5]. Using mass spectroscopy[5] the water desorption could be separated from the ammonia evolution. The number of ammonium sites and their decomposition temperatures were determined measuring thermal desorption curves. However, it was impossible to decide with mass spectroscopy, whether water molecules and ammonium ions are coupled on little covered zeolite surfaces. Furthermore, different IR absorption bands of the fundamental vibration modes were discriminated by means of the compensation method[6] giving information about the type of interaction of the ammonium ion with its surroundings and the force strength variation.

In this work the absorption bands of the NH_4^+ ion in Y-zeolite were studied more systematically for better understanding of the ammonium ion perturbation by hydrogen bridges with zeolites lattice or water molecules in its nearest vicinity.

MATERIAL AND METHODS

Linde NaY-zeolite (Si/Al = 2.4) was exchanged to 30%, 64% at 40°C and 96% NH_4^+ at 85 °C using NH_4Cl. A second exchange of the last sample with $CsCl_2$ conserved a residual NH_4^+ ion concentration of 36%. Originally, it was reported that the NH_4^+ ion is located in the sodalitic cage[1], a statement which is still under discussion. The mentioned three samples are termed $NaNH_4$(30%)-, $NaNH_4$(64%)- and $NaCsNH_4$(36%)-Y-zeolite.

A model 267 Perkin Elmer double bean IR spectrometer was used. Two IR cells, one in the reference beam, one in the sample beam, could be evacuated to 2×10^{-5}mb and heated to 450°C. The sample holder was a NaCl slice onto which zeolitic single crystals were deposited from an acetone slurry. The IR absorption measurements were started on a hydrated zeolite, then evacuated. The thermal treatments of the samples under vacuum at the temperatures noted in figures 1, 2 and 3 were applied for approximately 20 minutes. IR absorption bands were always recorded below 80 °C.

RESULTS

The distinct absorption bands of the samples are reproduced in figures 1 to 3. Two different absorption ranges are distinguished: a wide band between 3200 cm^{-1} and 2500 cm^{-1}, and a narrow absorption band around 1445 cm^{-1}. Apart from these bands a weak unstructured absorption near 2700 cm^{-1} could be detected at the $NaNH_4$(64%)-sample at very high water content. The wide band near 3500 cm^{-1} was attributed to the absorption of uncompensated zeolitic water. Spectral features are generally more pronounced at lower temperatures.

DISCUSSION

A comparison of the published absorption band positions of the unperturbed ammonium ion [4] at 3134 cm^{-1} and 1397

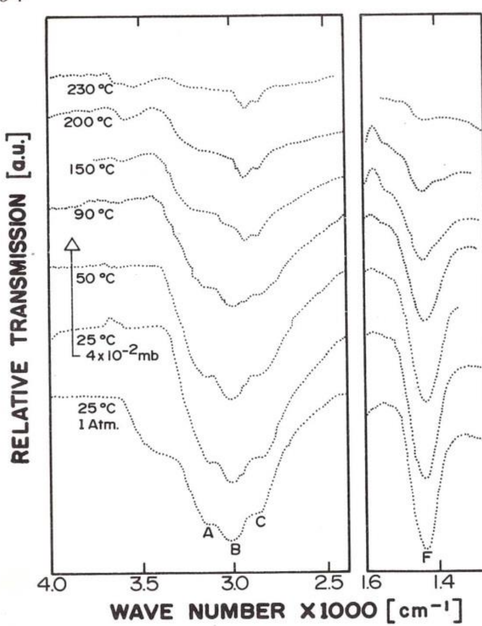


Figure 1: Infrared absorption of the ammonium ion of the $NaNH_4$ (64%)-Y-zeolite, reproduced in the spectrometer scales.

cm^{-1} with our data room temperature allows us to attribute the absorption around of 3000 cm^{-1} to υ_3 vibration modes of the perturbed NH_4^+ ion and the observed band near 1445 cm^{-1} to υ_4 modes. Both groups of the measured absorption bands are displaced with respect to reported data of the unperturbed ammonium ion, up to -340 cm^{-1} for the υ_3 vibration modes and +48 cm^{-1} for the υ_4 modes. These displacements are typical for hydrogen bridges[8], in this case between the ammonium ion protons and the oxygens of the zeolitic lattice, or the nearest water molecules. These band displacements also agree well in magnitude with published data[8]. Furthermore, the above mentioned weak ammonium ion peak near 2700 cm^{-1} confirm experimentally the presence of hydrogen bridges at least for highly water-loaded samples.

The absorption band near 3000 cm^{-1} can be deconvoluted into three subbands of nearly equal intensities (see figure 4). (The plotted relative absorption coefficient K permitted* us to resolve the total coefficient in a sum of partial coefficients due to the different band contributions). Using the least square method[3] to evaluate the quality of the subband superposition, a standard deviation of about 15% was found. Assuming a symmetry loss of the NH_4^+ ion caused by the hydrogen bridges, we postulate a removal of the triple degeneracy of the originally unperturbed ammonium ion which allows us to attribute each of the subbands to one of three υ_3 vibration modes.

Since all measurements were started with the zeolite samples of highest water content, we assign the broad width of the subbands to many water molecules in the surroundings of the ammonium ion. Different vibration energies of the three modes indicate a distinct effect of the hydrogen bridges on the vibration energy of each mode. Ammonium ion hydrogen bridges to neighboring water molecules are the predominant interaction of the NH_4^+ ion in the temperature range up to 100 °C.

The observed absorption bands generally lose intensity when the pressure in the IR cells was reduced and the sample temperature was increased (see figures 1 to 3). Both treatments decrease the water concentration of the zeolite in a temperature range where the ammonium ion is still thermally stable (see figure 5). We conclude that up to 100 °C the water-NH_4^+ ion interaction is the main reason for the high intensity of the IR absorption bands.

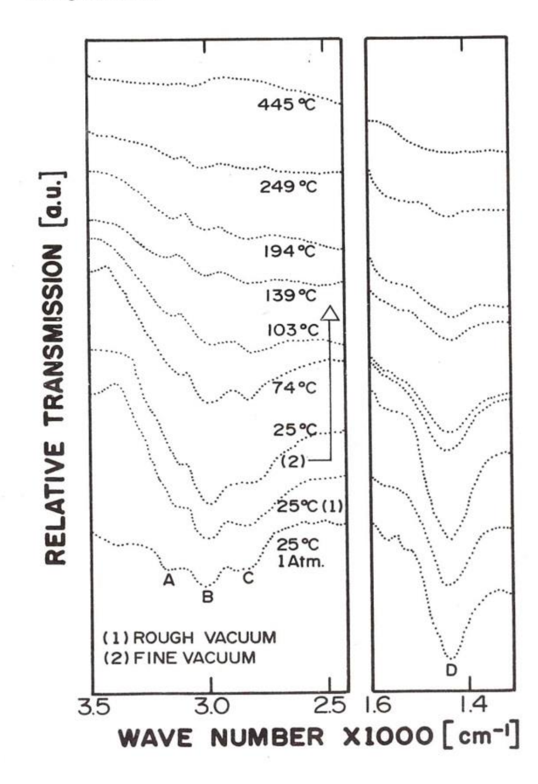


Figure 2: Infrared absorption of the ammonium ion of the $NaNH_4$ (30%)-Y-zeolite, reproduced in the spectrometer scales.

* The used relative absorption coefficient is defined by [7]: $K = \ln I_o/I$ and independent of any concentration measurement.

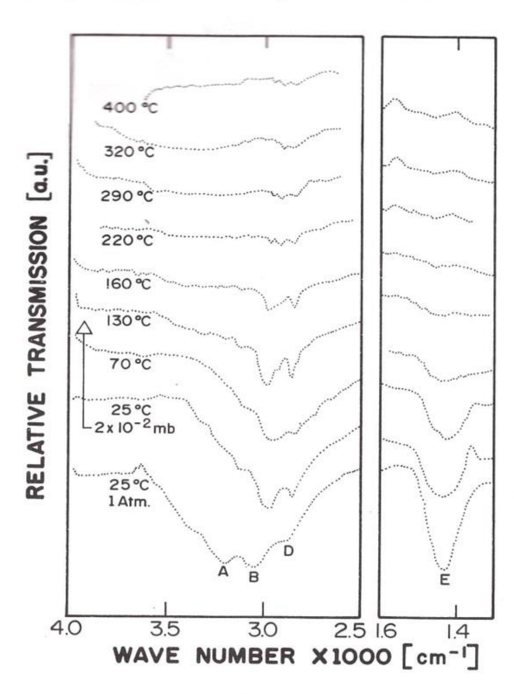


Figure 3: Infrared absorption of the ammonium ion of the $NaCsNH_4$ (36%)-Y-zeolite, reproduced in the spectrometer scales.

The simultaneous decrease of the ammonium ion concentration and the intensities at temperatures between 140 °C and 190 °C correlates with the NH_4^+ ion decomposition determined by mass spectrometric desorption measurements[4] (see figure 5). The mass spectrometric desorption curve presents a series of peaks which can be attributed to various desorption centers with different thermal stability caused by distinct interactions with their surroundings. In this case the majority of NH_4^+ ions are coupled with only one water molecule**. Although the measured desorption curves and the infrared experiment were not strictly done under the same experimental conditions***, we can assume that in the mentioned temperature range the gas pressure over the sample is nearly the same and, therefore, we are able to conclude that the ammonium ion is surrounded only by a very small number of water molecules, perhaps one or at the most two, in this temperature interval.

The $NaNH_4$(64%)-Y-zeolite and the $NaCsNH_4$(36%)-Y-zeolite present a notably different IR absorption between 2980 cm^{-1} and 2800 cm^{-1} at temperatures higher than 230 °C and 220 °C respectively. These absorptions can be again decomposed in three superimposed subbands with nearly the same peak positions (see table 1). This fact indicates that the cesium atoms do not influence notably the position of the new ammonium ion vibration modes, independently of where they are located in the lattice structure. The observed intensities and separations are significantly less than those at lower temperatures, therefore, the type of ammonium ion coupling must be different from those discussed above. Again, an inspection of the thermal desorption curve of the $NaNH_4$(64%)-Y-zeolite[6] explains the IR data where a nearly pure ammonia desorption was observed above 220 °C. We therefore assign the IR peaks to an ammonium ion anhydride which interacts only with the oxygen atoms of the zeolitic lattice. The small band displacements indicate hydrogen bridges with little difference in the bond energies between the distinct vibration modes. The low intensities of these bands make it difficult to determine whether there are three equal subbands.

The bandwidths of the subbands in the 3000 cm^{-1} region, which are between 260 cm^{-1} and 340 cm^{-1}, are considerably greater at room temperature than those at high temperatures, which are between 20 cm^{-1} and 60 cm^{-1}. To interpret this effect we must take into account that each observed subband is composed by a set of absorption lines of the same vibration mode. So, a broadening of the subbands can be caused either by a broadening of the lines or by an increase of their displacements. As the first alternative produces only a small effect on the total bandwidth, we have to assume enhanced line shifts to explain the broadened widths of the 3000 cm^{-1} subbands.

The high temperature absorption bands are not detectable in the $NaNH_4$(30%)-Y-zeolite. Over the whole temperature range measured only widely displaced absorption bands are recorded. This effect can be caused by too little intensities of the ammonium anhydride ion bands (the registered absorption is notably less intensive than that of the $NaNH_4$(64%)-Y-zeolite sample) or by a sufficiently high coupling of the water

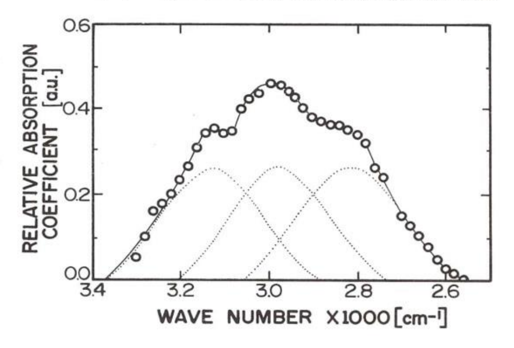


Figure 4: Relative absorption coefficients of the absorption bands near 3000 cm^{-1} of the ammonium ion of the $NaNH_4$(30%)-Y-zeolite as a function of the wave number at normal conditions.

** Hunger, M., Espaillat, H. and Martinez-D'Alessandro, A., unpublished data.

*** The thermal desorption curves were measured with cylindrical samples of about 1/2 cm^3 with a gas pressure of about $2x10^{-2}$mb over the sample, increasing stepwise its temperature similar to the IR measurements.

TABLE 1
Positions of the absorption band maxima of the
$NaNH_4$ (64%)-, $NaNH_4$ (30%)- and $NaCsNH_4$ (36%)-Y-zeolites, given in cm^{-1}.

Zeolite	Low Temp.(10^{+3}mb)			Medium Temp. (10^{-2}mb)			High Temp. (10^{-2}mb)		
NH_4(64%)	3130	3000	2840	- - -	- - -	- - -	2970	2920	2840
NH_4(30%)	3180	3010	2860	- - -	- - -	- - -	- - -	- - -	- - -
NH_4(36%)Cs	3180	3030	2880	3110	2980	2840	2960	2910	2840

Figure 5: Relative absorption coefficients of the absorption bands near 3000 cm^{-1} (□) and near 1445 cm^{-1} (Δ), and the residual concentration[5] (o) of the $NaNH_4$(64%)-Y-zeolite as a function of the sample temperature.

molecules in the nearest surroundings of the NH_4^+ ion. (Unfortunately, a mass spectrometric desorption curve is not available yet to check this supposition). As no ammonium anhydride bands are found, only the low temperature band positions are listed in table 1.

The above discussed subbands cannot be assigned to different adsorption sites: in such a case, a stepwise cancellation of these subbands would be expected with increasing temperature. That three absorption bands are always detected in the 3000 cm^{-1} region (both in the low and in the high temperature range) indicate a continued suppression of the original ammonium ion vibration degeneracy. This effect is caused by the variation of the NH_4^+ ion symmetry possibly generated by hydrogen bridges formed with the oxygens of the water molecules or zeolitic surface.

Although the absorption bands near 1445 cm^{-1} show normally no detectable structure, we have to assume a splitting of these bands too, because of the removal of the degeneracy of the vibration modes, which is general concept. Nevertheless, in a special case the supposed effect can be detected in the $NaCsNH_4^+$(36%)-Y-sample where the registered absorption shows little structure in the temperature region of about 130 °C. Unfortunately, as it can be seen in the absorption range near 3000 cm^{-1} (see figure 3), in the mentioned temperature region a superposition of two spectra occurs hence preventing an exact analysis of the spectrum. A hypothetic decomposition of the absorption of the $NaNH_4^+$(30%)-Y-sample at room temperature allows us to estimate the order of magnitude of the shift between the subbands in about 20 cm^{-1}, i.e., notably less than the observed up to 340 cm^{-1} in the 3000 cm^{-1} region.

The above data leads to the following interpretation of the absorption bands of the $NaCsNH_4$(36%)-Y-zeolite in the temperature range between 25 °C and 160 °C (see Figure 3). This absorption is characterized by three well separated bands near 3130 cm^{-1}, 2980 cm^{-1} and 2850 cm^{-1} with different intensities (neglecting the shoulder at 2930 cm^{-1} and taking into account the increasing intensity of the band near 2850 cm^{-1} caused by the superposition of the observed absorption at higher temperature). The new absorption is characterized by intermediate band positions (see table 1), bandwidths and intensities of the absorption bands (see figure 3). This band type is not observable in the cesium free zeolite samples and therefore it must be generated by the realized NH_4^+-Cs exchange. The recorded uneveness in the band intensities and

the band widths indicate high asymmetric perturbation of the ammonium ion. If this effect is caused directly by the cesium atom in the nearest NH_4^+ ion vecinity or it is only a consequence of lattice deformations, cannot be currently decided.

ACKNOWLEDGEMENTS

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